

Why is $P2_1/n$ a Standard Non-Standard Space Group?

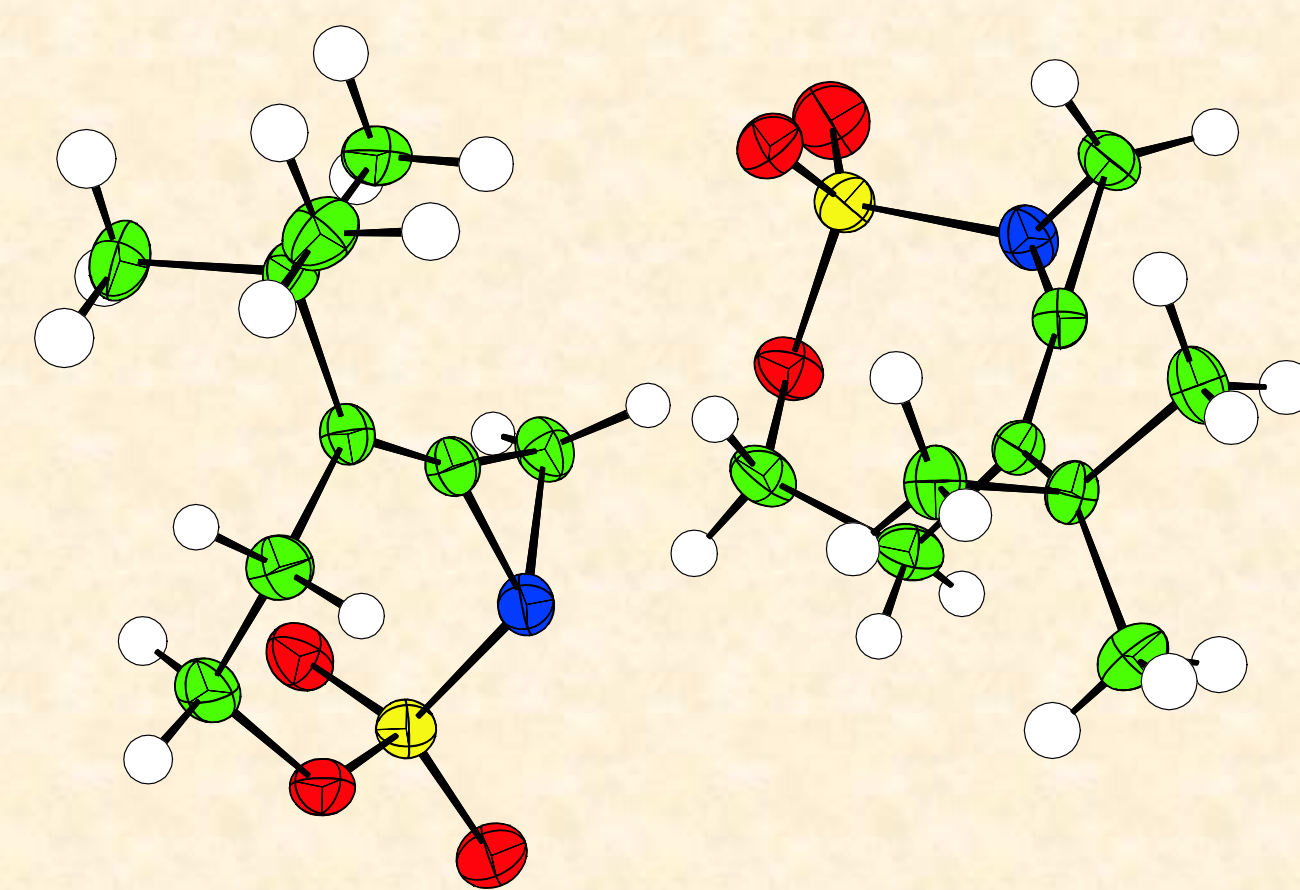
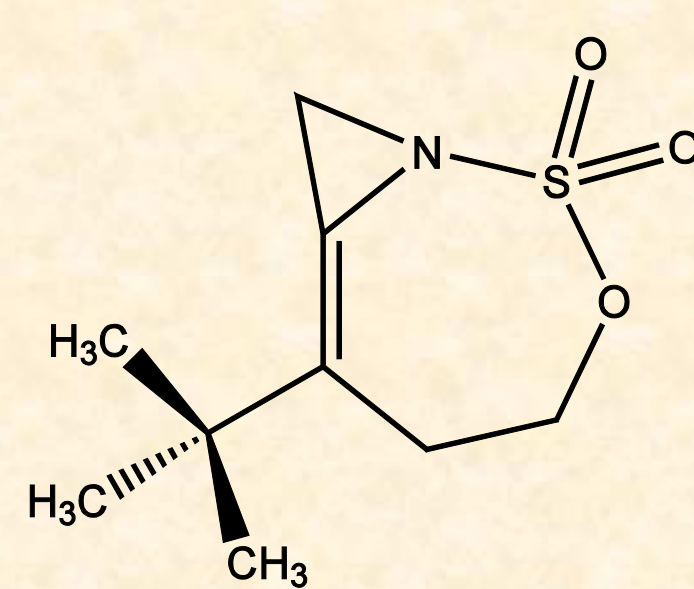
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An Unusual Methylene Aziridine

- A number of methylene aziridines were prepared during a study of nitrogen-containing 1,3-dipoles^{1,2} in order to probe their potential as 2-aminoallyl cation precursors.³
- The structure of 6-tert-butyl-3-oxa-2-thia-1-azabicyclo-[5.1.0]oct-6-ene 2,2-dioxide was determined.⁴
- Structure details:
 - Monoclinic, space group $P2_1/n$
 - $a = 13.8593(3)$ Å, $b = 10.5242(2)$ Å, $c = 14.8044(4)$ Å and $\beta = 92.0014(7)^\circ$.
 - Solved with SIR92⁵ and refined with CRYSTALS.⁶
 - Two molecules in the asymmetric unit ($Z'=2$).



- The IUCr online utility checkCIF gives the following Alert:

PLAT128_ALERT_4_G

Non-standard setting of Space-group $P21/c$. . . $P21/n$

and explains further:

'The reported monoclinic space-group is in a non-standard setting. Transformation to the conventional setting is indicated unless there is a good (scientific) reason not to do so.'

What does this mean? Should the unit cell be transformed?

Transforming from $P2_1/n$ to $P2_1/c$

- $P2_1/n$ and $P2_1/c$ are different cell settings of The World's Favourite Space Group, Number 14.
- The cell parameters were transformed by the matrix:

$$A = \begin{pmatrix} 1 & 0 & 0 \\ 0 & \bar{1} & 0 \\ \bar{1} & 0 & \bar{1} \end{pmatrix}$$

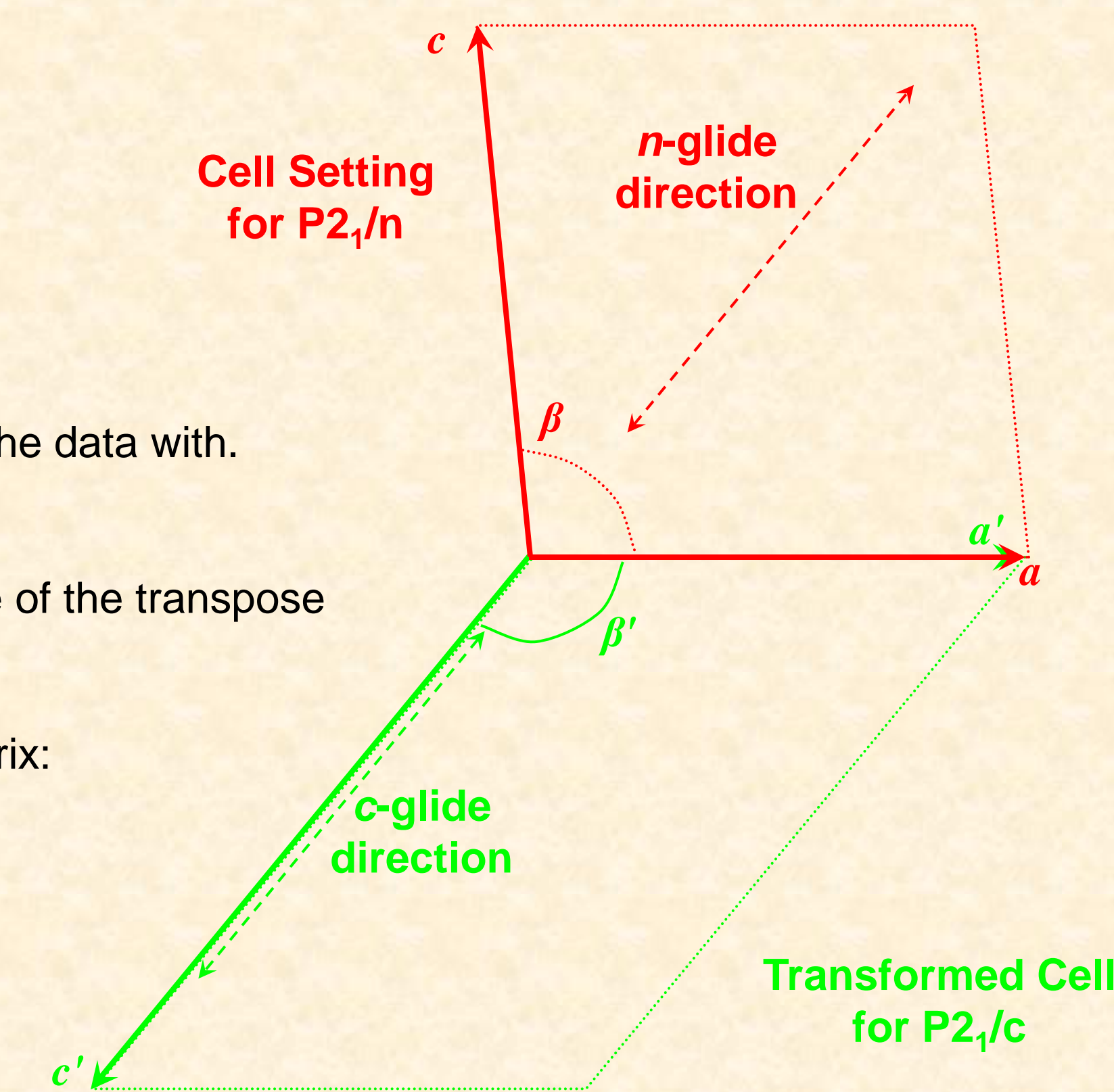
giving a new cell of the same volume to re-integrate the data with.

- The matrix to transform the coordinates is the inverse of the transpose of that used to transform the cell.
- The atomic coordinates were transformed by the matrix:

$$(A^{-1})^T = \begin{pmatrix} 1 & 0 & \bar{1} \\ 0 & \bar{1} & 0 \\ 0 & 0 & \bar{1} \end{pmatrix}$$

and the structure re-refined.

- The final cell was $a = 13.8594(2)$ Å, $b = 10.5243(2)$ Å, $c = 19.9230(3)$ Å and $\beta = 132.0439(7)^\circ$.
- The new cell is very oblique compared to that of the original cell which was approximately orthogonal.



Differences Between $P2_1/n$ and $P2_1/c$

- It has long been known that refinements in oblique cells have increased correlation between selected parameters, potentially making refinements less stable.⁷ Thus, a large β value would be expected to give increased correlation between parameters with respect to the a and c axes.
- In $P2_1/n$, the largest correlations are between the sulphur atomic displacement parameters (ADPs) and the scale factor. In $P2_1/c$, the correlations between the sulphur ADPs and the scale factor are of a similar magnitude, but the correlations between individual components of the ADPs are greater, e.g. the largest correlation which is 0.809 between $U_{33}(O14)$ and $U_{13}(O14)$ compared with 0.080 for the $P2_1/n$ refinement.
- Correlations between the positional parameters are also affected; though the changes are smaller, the effects are visible by comparing the s.u. values for derived parameters calculated with and without covariances.
- Only the variances are included in the CIF, so it is easy to calculate the s.u. values for derived parameters calculated without covariances using PLATON.⁸ These can be compared with the values calculated using the full variance covariance matrix (i.e. using the CIF produced by CRYSTALS).

Selected bond-lengths with s.u.s

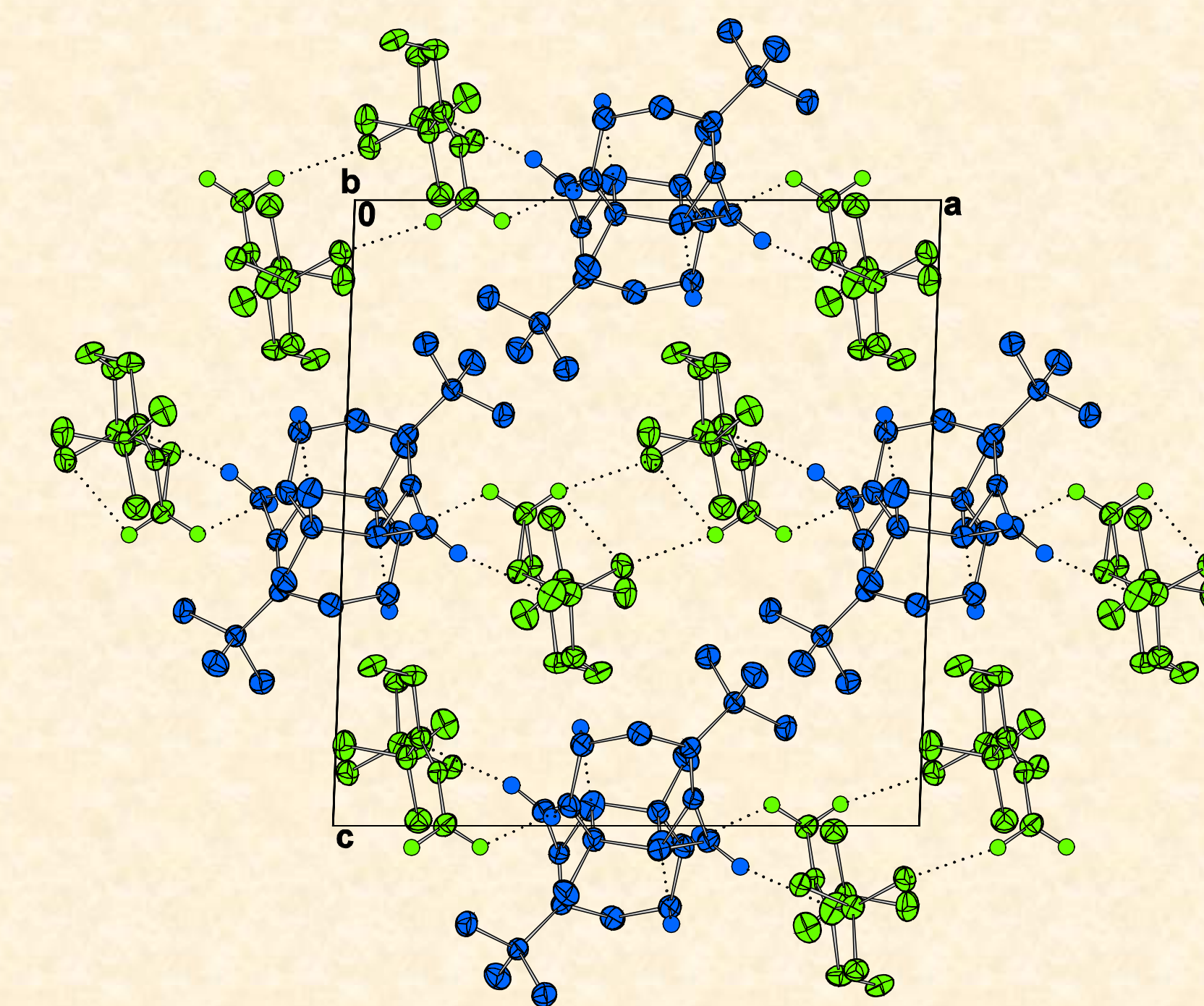
	CRYSTALS		PLATON	
	In $P2_1/n$	In $P2_1/c$	In $P2_1/n$	In $P2_1/c$
S1—O2	1.4271(16)	1.4278(17)	1.4272(17)	1.428(2)
S1—O3	1.5569(16)	1.5573(16)	1.5570(16)	1.5574(16)
S1—N8	1.6524(18)	1.6527(18)	1.6523(18)	1.653(3)
S1—O14	1.4182(16)	1.4189(17)	1.4182(17)	1.4189(19)
C10—C11	1.532(3)	1.533(3)	1.532(3)	1.533(3)
C10—C12	1.538(3)	1.540(3)	1.538(3)	1.540(4)
C10—C13	1.528(3)	1.529(3)	1.528(3)	1.528(6)
S101—O103	1.5628(16)	1.5628(16)	1.5628(16)	1.5629(19)
S101—N108	1.6577(18)	1.6571(18)	1.6576(19)	1.657(3)
S101—O114	1.4200(18)	1.4204(18)	1.4201(19)	1.420(2)
S101—O102	1.4252(18)	1.4262(18)	1.4252(18)	1.4262(19)
O103—C104	1.475(3)	1.474(3)	1.475(3)	1.474(3)
C104—C105	1.515(3)	1.514(3)	1.515(3)	1.514(5)
C105—C106	1.525(3)	1.525(3)	1.525(3)	1.524(4)
C106—C107	1.317(3)	1.316(3)	1.318(3)	1.316(3)

Selected Correlations

	In $P2_1/n$	In $P2_1/c$
Largest correlations when in $P2_1/n$:		
OSF / $U_{11}(S1)$	0.365	0.317
OSF / $U_{22}(S1)$	0.361	0.310
OSF / $U_{33}(S1)$	0.353	0.312
OSF / $U_{11}(S101)$	0.357	0.307
OSF / $U_{22}(S101)$	0.343	0.297
OSF / $U_{33}(S101)$	0.354	0.307
Largest correlations when in $P2_1/c$:		
$U_{11}(C13)$ / $U_{13}(C13)$	0.010	0.801
$U_{33}(C13)$ / $U_{13}(C13)$	0.023	0.805
$U_{11}(O14)$ / $U_{13}(O14)$	-0.091	0.804
$U_{33}(O14)$ / $U_{13}(O14)$	-0.080	0.809
$U_{11}(C111)$ / $U_{13}(C111)$	0.004	0.781
$U_{33}(C111)$ / $U_{13}(C111)$	0.002	0.782
$U_{11}(O102)$ / $U_{13}(O102)$	-0.042	0.795
$U_{33}(O102)$ / $U_{13}(O102)$	-0.034	0.797

So, $P2_1/n$ and $P2_1/c$?

- The bond lengths are very similar for the refinements in both cell settings whether determined by PLATON or CRYSTALS; slight differences are because in refinement software numbers are stored with full 32 bit, floating-point precision, whereas software that reads a CIF is limited to the decimal representation in the file.
- The s.u. values for all the C—C and C—O bonds are also consistent when calculated using the full variance-covariance matrix, regardless of whether it is refined in $P2_1/n$ or $P2_1/c$.
- Calculations using only the variances give a good estimate of the s.u. values when the structure is refined in $P2_1/n$ (i.e. with the more orthogonal cell).
- The corresponding s.u. calculations in $P2_1/c$ (with the more oblique cell) are less reliable when the covariances are excluded.
- This effect is most apparent where the bond is predominantly parallel to the a axis (which is unaffected by the cell transformation) where the s.u. values are nearly doubled (e.g. S101—N108, C104—C105 and C10—C13).
- Thus, excluding the covariances from calculations of the s.u. values has a much larger effect for monoclinic structures in a unit-cell setting where β deviates significantly from 90° .
- The increase in the correlation due to the oblique cell setting is also apparent, and although there are no obvious consequences in this case, this could give rise to refinement difficulties for more complex structures and in the case of powder diffraction data, this effect might be expected to be enhanced.
- In conclusion, there are good scientific reasons for choosing to use the "more orthogonal" monoclinic setting, in this case, $P2_1/n$ instead of $P2_1/c$.



The crystal packing (in $P2_1/n$), viewed down the b axis, showing two residues in green and blue C—H...O interactions are shown as dotted lines.

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